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Heterogeneous Catalysis with Basic Compounds to Achieve the Synthesis and C–N Cleavage of Azetidin-2-ones under Microwave Irradiation

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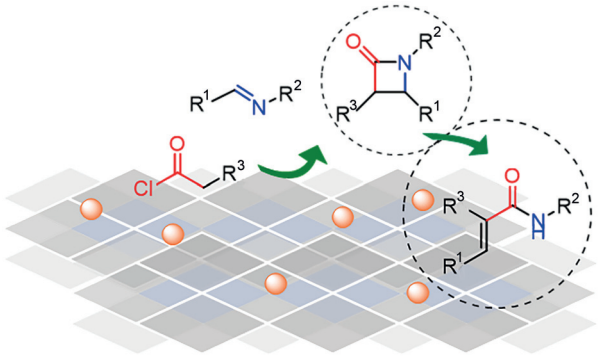

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Abstract The synthesis of azetidin-2-ones with a completely heterogeneous catalysis is reported. The use of basic compounds as solid catalysts allowed for the synthesis of azetidin-2-ones under microwave irradiation without organic additives such as triethylamine. An excellent catalyst for this transformation was Mg-Al hydroxide (MAH). The present methodology offers the advantages of non-hazardous reaction conditions, short reaction times, high yields, and catalyst reusability. Different substitution groups were tested on the imines and acyl chlorides to explore the scope of the reaction. Unconventional N–C4 bond cleavage was detected in azetidin-2-ones. MAH was characterized by N_2 adsorption–desorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HR-TEM).

Key words heterogeneous catalyst, Mg-Al hydroxide, azetidin-2-ones, ring opening, microwave irradiation

Many antibiotics, including penicillin, have the azetidin-2-one (β-lactam) structure, which has been known in the field of medicinal chemistry since 1940.[1,2] Considerable research efforts have focused on this kind of heterocycle[3] to develop potent cholesterol absorption inhibitor **1**,[4,5] prostate-specific antigen inhibitor **2**,[6,7] antiproliferative agent **3** that acts by inhibition of tubulin polymerization,[8–10] and inhibitor **4** of the human cytomegalovirus protein[11] (Figure 1).

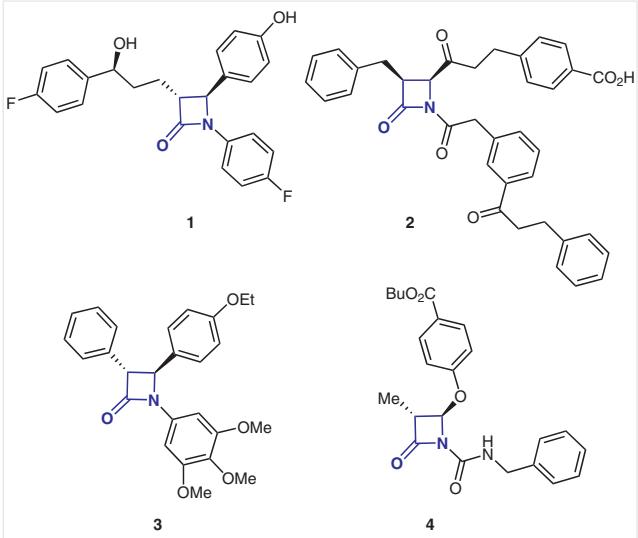


Figure 1 Structures with an azetidine-2-one nucleus that have biological activity

Given the relevance of this structure, the development of new procedures for the creation of azetidin-2-one-based series of synthetic compounds should certainly be instrumental in the search for novel drugs. Several methodologies have been developed for the construction of four-membered nitrogen heterocycles.[12–21] The Staudinger synthesis, starting from ketene-imine, has been one the most popular

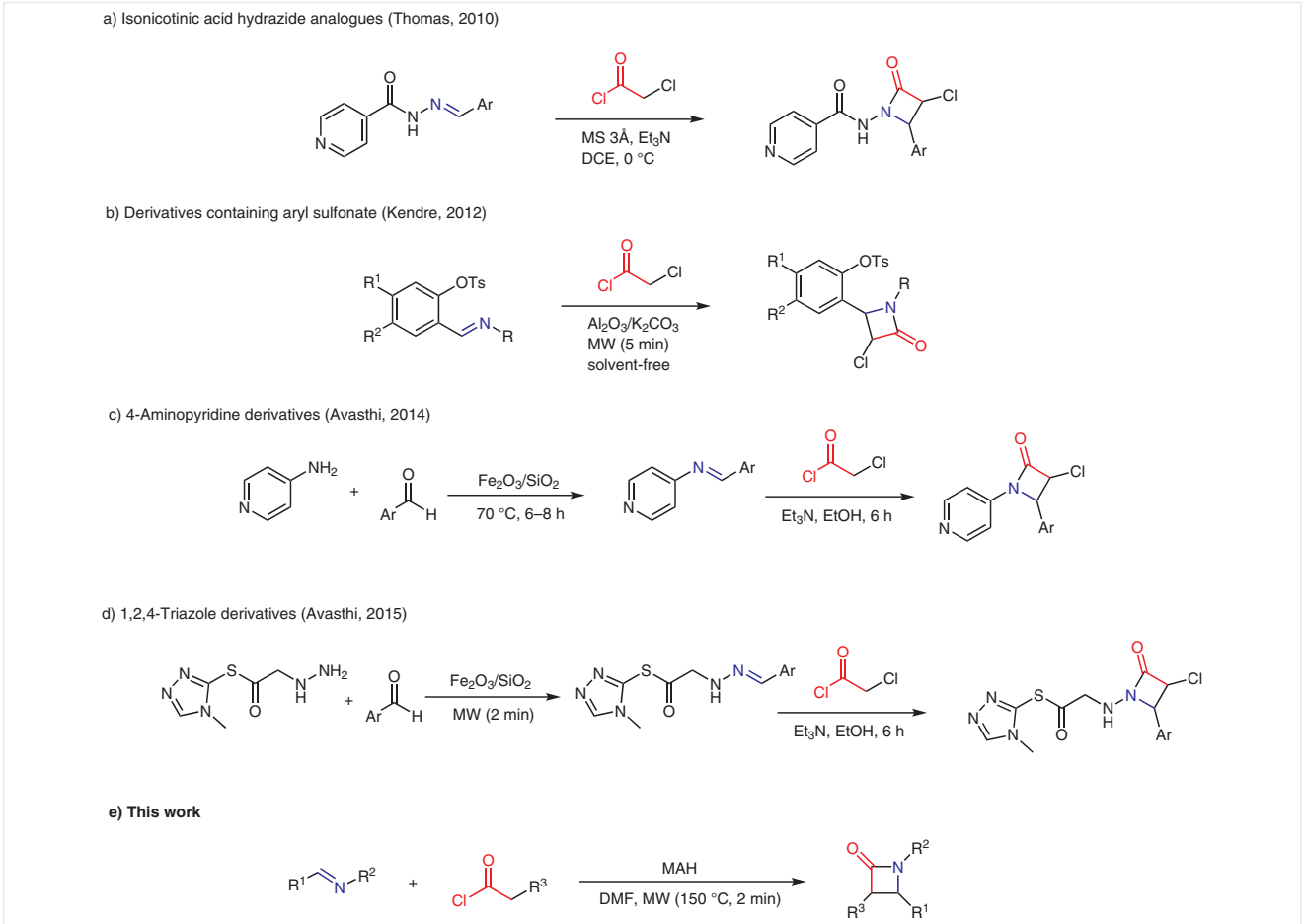
classical methods.[22] Among other methodologies are the [2+2] cycloaddition of isocyanates to vinyl ethers,[23] the ester or amide enolate-imine condensations,[24] and recently the Kinugasa reaction.[25] Each of these methodologies has been developed and implemented to improve selectivity, increase yield, and attain shorter reaction times. However, most of them are based on homogeneous catalysis with organic bases, representing an important drawback.

Heterogeneous catalysis is desirable in industry because the product purification process is simplified, in part by the ease of handling solid catalysts. Moreover, the catalysts can be recovered and reused.[26–30] Basic compounds such as Al_2O_3, MgO, basic zeolites, and laminar hydroxides have been successfully employed in heterogeneous catalysis to achieve various organic transformations, including decarboxylation reactions,[31] pyranpyrazole synthesis,[32] methylation reactions,[33] and condensations.[34] In this context, extensive research on Mg-Al hydroxide (MAH) has led to its application in the synthesis of amides[35] and coumarins,[36] as well as in a variety of fundamental reactions: oxidation,[37] hydroxylation,[38] olefin epoxidation,[39] and transesterification.[40]

It is possible to synthesize azetidin-2-ones in the presence of diverse solid materials, including MS 3Å,[41] Fe_2O_3/SiO_2,[42,43] and Al_2O_3[44] (Scheme 1).

Azetidin-2-ones have been synthesized with inorganic materials and homogeneous catalysis, using compounds such as triethylamine[45] (Scheme 1a, c, d) and K_2CO_3[44] (Scheme 1b). To the best of our knowledge, their synthesis with a purely heterogeneous methodology has yet to be reported. We presently describe reactions between imines and acyl chlorides carried out with heterogeneous catalysis and microwave irradiation (Scheme 1e).

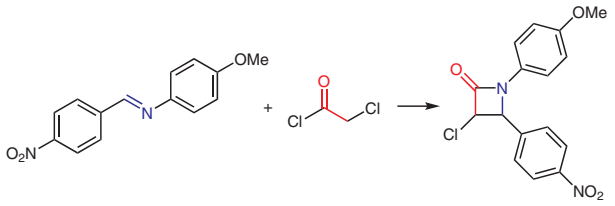
As a model system for optimizing the synthesis of azetidin-2-ones, *N*-(4-nitrobenzylidene)-4-methoxyaniline (**5j**) and 2-chloroacetyl chloride (**6a**) were reacted under microwave irradiation (Table 1). Evaluation was made of the effect of various solvents, including MeCN, PhMe, DMF, and THF (Table 1, entries 1–4), all at 150 °C except the latter. Performing the reaction in MeCN or PhMe afforded the desired product in low yield (entries 1 and 3). With DMF (entry 4), a moderate yield was obtained for **7j** (65%). This compound was also achieved in a lower yield (37%) by re-



Scheme 1 Approaches for the synthesis of azetidin-2-ones with solid materials

acting **5j** and **6a** under neat conditions (entry 5). As a reference, triethylamine was used under similar conditions (entry 6), giving **7j** in a low yield (33%).

Table 1 Optimization of the Synthesis of Azetidin-2-one **7j**[a]



5j **6a** **7j** (*cis/trans*)

Entry	Solvent	Catalyst	Temp (°C)	Time (min)	Ratio[b] (*cis*/*trans*)	Yield (%)
1	MeCN	–	150	120	41/59	49
2	THF	–	65	30	trace	trace
3	PhMe	–	150	120	47/53	38
4	DMF	–	150	150	46/54	65
5	–	–	150	180	22/78	37
6[c]	DMF	Et_3N	150	120	45/55	33
7[d]	DMF	MgO	150	120	52/48	61
8[d]	DMF	γ-Al_2O_3	150	120	trace	trace
9[d]	DMF	MAH	150	120	53/47	76
10[e]	DMF	MAH	150	2	52/48	95
11[e]	DMF	MAH	100	2	52/48	50
12[e]	DMF	MAH	70	2	52/48	30

[a] Reaction conditions: **5j** (0.2 mmol), **6a** (0.21 mmol), sealed vessel, and microwave irradiation.
[b] The *cis*/*trans* ratio was calculated from the ^{1}H NMR spectrum of the reaction crude and GC-MS.
[c] In open vessel with 10% mol of base.
[d] In open vessel with 10% w/w of inorganic material.
[e] In sealed vessel with 10% w/w of inorganic material.

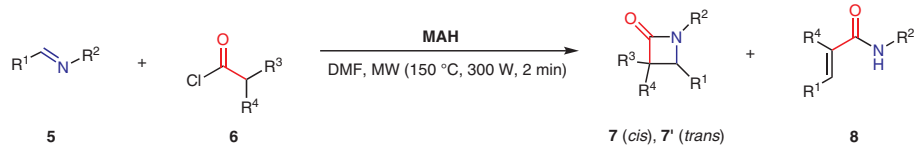
The next step was the examination of catalytic materials (Table 1, entries 7–12), finding pure magnesium oxide (MgO, entry 7) slightly active and aluminum oxide (γ-Al_2O_3, entry 8) inactive. Testing MAH under the same reaction conditions increased the yield to 76% (entry 9), and then to 95% by shortening the reaction time from 2 hours to 2 minutes (entry 10). When conducting the reaction at different temperatures, a significantly reduced yield was observed below 150 °C (entries 11 and 12). Finally, the azetidin-2-one **7j** (entry 10) was purified by column chromatography with a hexane/EtOAc mixture.

After optimizing the reaction conditions, the scope of the reaction was explored with a variety of imines (Table 2). The presence of an aromatic moiety did not affect the yield. All the imines were excellent substrates regardless of the presence of electron-donating or electron-withdrawing groups on the benzene rings. The yields found with different derivatives of acetyl chloride depended on the electronegativity of the substituent at the α-position to the carbonyl group. With the presence of two chlorines, the transformation towards azetidine-2-one was quantitative (Table 2, entries 18–20). The yield decreased when using the acetyl chloride with an acetoxy group as a substituent. This transformation required prolonged reaction times (10 min), which led to the hydrolysis of the imine and the generation of by-products (entry 22).

There was also a low yield for entries 2, 5, 6, 8, 9, 11, and 15, attributed to ring-opened product **8** (discussed in detail later). A mixture of *cis*/*trans*-isomers was formed in all experiments, in agreement with the literature.[46] The *cis*/*trans* ratio was determined by NMR and GC-MS analysis of the reaction crude. Overall, slightly lower diastereoselectivity was observed for reactions with electron-donating groups on the *trans*-isomer. On the other hand, the presence of electron-withdrawing groups on the aryl moiety afforded the *cis*-isomer as the major product. Likewise, N-acetate- and N-hexanoate-substituted azetidin-2-ones were obtained in good yield and, surprisingly, with only one isomer (Table 2, entries 16 and 17). The structural description for the *cis*-isomer (J = ~5.0 Hz; dihedral angle 0°) and *trans*-isomer (J = ~2.0 Hz; dihedral angle 139.9°) is given as a coupling constant, provided by NMR and X-ray crystal structure analysis of product **7j** (Figure 2).

Another compound was isolated in some experiments. After characterization and confirmation by X-ray structural analysis (Figure 2c), it was identified as the ring-opened product (Figure 3). The well-known core reactivity of azetidin-2-one[23] owes itself to its strain energy, which results in four reactive positions on the nucleus of these compounds. Selectivity depends on the electronic effects of substituents and the reaction conditions. The cleavage of the N–C4 bond is typically carried out by hydrogenolysis when the C-4 substituent is an aryl group.[47] The photo-induced electron transfer methodology has been applied as well.[48] Cleavage is also found when the substituent is other than an aryl group, as in the reaction between 4-formyllactams and 2-(trimethylsilyl)thiazole.[49] The behavior observed presently is distinct from that reported previously. MAH herein catalyzed the ring opening, leading to different yields of the C4–N cleavage derivatives **8** (Figure 3). Unfortunately, no tendency was detected in the reaction conditions or for the electronic nature of substituents.

Table 2 Synthesis of Azetidin-2-ones **7** by Using Heterogeneous Catalysis with MAH

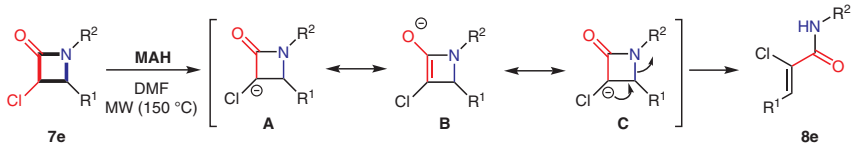


5 **6** **7** (*cis*), **7'** (*trans*) **8**

Entry	R^1	R^2	R^3	R^4	Ratio[a] (*cis*/*trans*)	Yield (*cis*/*trans*, %)[b]	**8** (%)[c]
1	Ph	Ph	H	Cl	**7a** (43/57)	40/52	n.d.
2	4-$MeOC_6H_4$	Ph	H	Cl	**7b** (40/60)	36/53	10
3	4-$O_2NC_6H_4$	Ph	H	Cl	**7c** (55/45)	47/38	n.d.
4	4-FC_6H_4	Ph	H	Cl	**7d** (42/58)	39/54	n.d.
5	Ph	4-$O_2NC_6H_4$	H	Cl	**7e** (49/51)	29/29	25
6	Ph	4-BrC_6H_4	H	Cl	**7f** (43/57)	25/33	34
7	3-ClC_6H_4	4-ClC_6H_4	H	Cl	**7g** (63/37)	55/32	n.d.
8	2-thienyl	4-ClC_6H_4	H	Cl	**7h** (51/49)	22/22	39
9	2-furanyl	4-ClC_6H_4	H	Cl	**7i** (0/0)	0/0	40
10	4-$O_2NC_6H_4$	4-$MeOC_6H_4$	H	Cl	**7j** (59/41)	55/40	n.d.
11	4-$MeOC_6H_4$	4-$MeOC_6H_4$	H	Cl	**7k** (40/60)	46/31	12
12	4-$MeOC_6H_4$	4-ClC_6H_4	H	Cl	**7l** (53/47)	46/40	n.d.
13	4-$O_2NC_6H_4$	4-$MeOC_6H_4$	H	Br	**7m** (65/35)	55/0	n.d.
14	2,4-ClC_6H_3	4-ClC_6H_4	H	Cl	**7n** (74/26)	42/43	n.d.
15	$C_6H_5CH{=}CH$	4-$MeOC_6H_4$	H	Cl	**7o** (47/53)	26/32	38
16	4-FC_6H_4	MeO_2CCH_2	H	Cl	**7p** (0/100)	0/82	n.d.
17	4-FC_6H_4	$MeO_2C(CH_2)_5$	H	Cl	**7q** (0/100)	0/80	n.d.
18	4-$O_2NC_6H_4$	4-$MeOC_6H_4$	Cl	Cl	**7r** (99)	91/0	0
19	4-$MeOC_6H_4$	4-$MeOC_6H_4$	Cl	Cl	**7s** (99)	83/0	0
20	2,4-ClC_6H_3	4-ClC_6H_4	Cl	Cl	**7t** (98)	89/0	0
21	2,4-ClC_6H_3	4-ClC_6H_4	H	Br	**7u** (55/45)	38/32	n.d.
22	4-$O_2NC_6H_4$	4-$MeOC_6H_4$	H	OAc	**7v** (54/46)	12/10	n.d.

[a] The *cis*/*trans* ratio was ascertained by GC-MS analysis of the reaction crude.
[b] Isolated yield.
[c] n.d.: Not detected.

Thus, several experiments were performed to gain insight into the reactivity of azetidin-2-ones and MAH. A mixture of stereoisomers of **7e** (*cis*/*trans*) was used under the same reaction conditions (Table 2), monitoring reaction crudes with GC-MS. The analysis revealed that MAH induces the opening of the heterocycle to provide **8e** in moderate yield (50%). A proposal for the mechanism is outline in Scheme 2. The basic characteristics of MAH are responsible for activating the α-proton to the carbonyl group, which may be stabilized by resonance structures (A ↔ B) to later generate the ring-opened product.



7e **A** **B** **C** **8e**

Scheme 2 Azetidin-2-one ring opening catalyzed by MAH

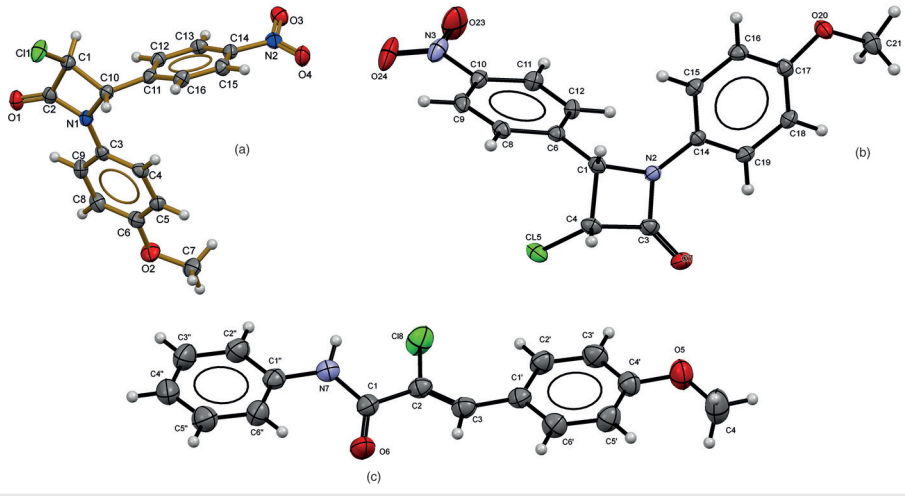


Figure 2 ORTEP drawing of compound **7j** for the: a) *trans*-isomer, b) *cis*-isomer, and c) ring-opened product **8b**

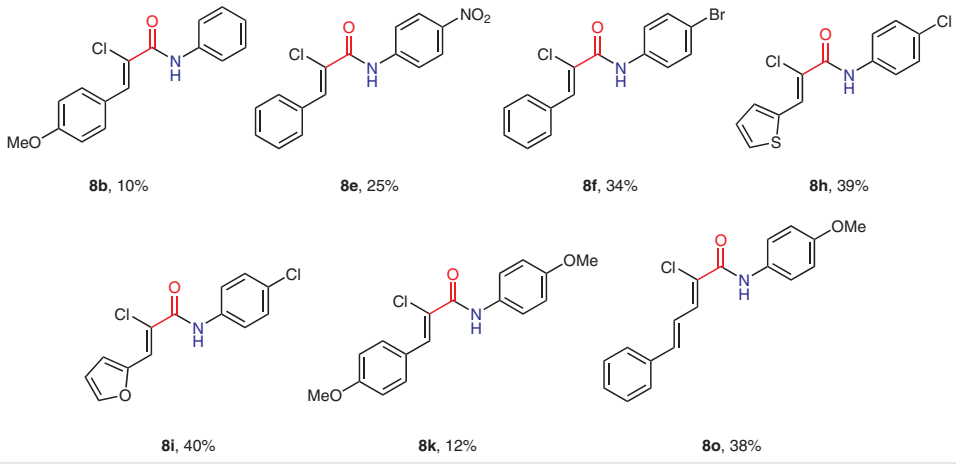
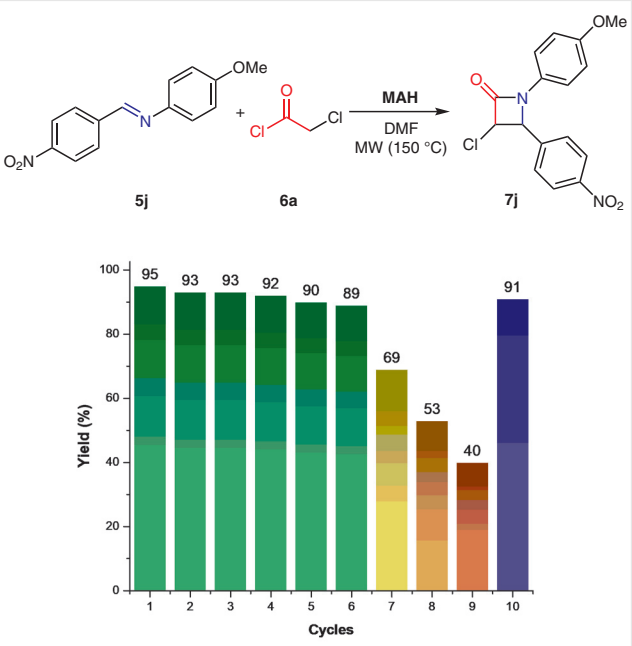


Figure 3 The products isolated and corresponding yield that resulted from the ring opening

The test of catalyst reuse was conducted with the imine **5j** (Scheme 3) under the previously established optimal conditions (*vide supra*). Once the first run was completed, the MAH catalyst was filtered in vacuo and then washed with dichloromethane. The recovered catalyst was reused directly (without the need for stove drying) in further cycles under the same conditions. The MAH catalyst could be recovered and reused up to 6 times without any significant loss of catalytic activity. According to the monitoring of the reaction crude by GC-MS, an 89% yield of **7j** was obtained on the 6th run (Scheme 3). The catalytic activity decreased dramatically by the 9th cycle, giving only a 40% yield. However, it could be recovered by washing the catalyst with water and drying it at 120 °C for 10 minutes, resulting in 91% yield.

The synthesis of MAH was carried out by the typical co-precipitation procedure.[50] The textural properties of MAH were characterized by N_2 physisorption analysis at 77 K (Figure 4a). The measured surface area of BET (232 m^2/g) was superior to that of MgO (45 m^2/g), with a pore volume of 0.60 cm^3/g and a pore diameter of 7.5 nm. According to the powder X-ray analysis, the predominant phase in MAH is boehmite (JCPDS card 21-1307), which is an aluminum oxyhydroxide (Figure 4b). The scanning electron microscope (SEM) and transmission electron microscopy (TEM) analyses revealed that MAH had an amorphous character, a fibrillar shape, and a particle size under 1 µm (Figure 4c, d).



Scheme 3 Recycling the MAH catalyst. *Reagents and conditions*: **5j** (0.2 mmol), **6a** (mmol), MAH (10% w/w), DMF (3 mL) in open vessel and microwave irradiation at 150 °C. The conversion was calculated from GC-MS of the reaction crude.

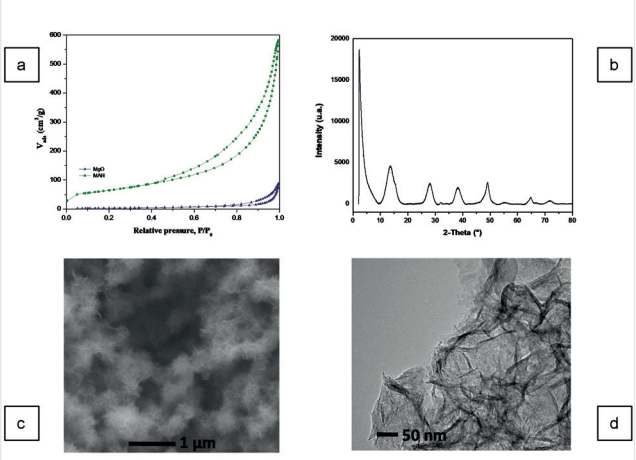


Figure 4 MAH characterization by: a) an N_2 adsorption–desorption graph, b) an X-ray diffractogram, and images from c) scanning electron microscopy (SEM) and d) transmission electron microscopy (TEM).

In conclusion, the use of heterogeneous catalysis with MAH resulted in the development of an efficient and environmentally benign strategy for synthesizing azetidin-2-one derivatives without the aid of organic bases. This methodology offers several advantages, including high yields, short reaction times, low cost, and a relatively clean reaction profile. The catalyst could be synthesized simply and recycled up to six times without any significant decrease in activity. Subsequently, catalyst recovery was characterized by effortless regeneration of activity. Azetidin-2-one ring-opened products were formed through N–C4 bond cleavage promoted by the MAH catalyst.

Microwave irradiation was conducted in a Discover SP CEM microwave apparatus. The progress of the reaction was monitored by TLC (aluminum sheets, silica gel 60 F/UV_{254}), using a hexane/EtOAc mixture as eluent. Visualization was carried out with UV light and I_2. The products were purified by column chromatography over silica gel (MN Kieselgel 60, 230–400 mesh). ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 MHz, Varian Gemini 300 MHz, or Bruker Ultrashield 500 and 600 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm, relative to TMS and $CHCl_3$ as the internal standard. Melting points were determined on a digital Electrothermal 90100 melting point apparatus. High-resolution mass spectra (HRMS) were obtained with electrospray ionization on a Bruker QTOF mass spectrometer. X-ray data were collected on an Oxford Diffraction Gemini 'A' diffractometer with a CCD area detector. N_2 physisorption samples were dried overnight at 120 °C, degassed at 200 °C under N_2 flow for 3 h and examined at 77 K in Micromeritics Tristar II Plus 3030. The BET surface was measured in the relative pressure range of 0.05–0.3. Powder X-ray diffraction was obtained in a PANalytical X Pert Pro MRD diffractometer with Cu Kα radiation. Particle morphology was analyzed by TEM on a JEOL JEM-100S and by SEM on a JEOL 5900 LV.

^1H and ^{13}C NMR Spectra: For the numbering of carbon atoms, see the Supporting Information.

Preparation of Catalysts; General Procedure

γ-Al_2O_3

γ-Al_2O_3 was synthesized by the precipitation method. A solution of $Al_2(SO_4)_3{\cdot}17H_2O$ in deionized H_2O was prepared in a 1:12 mass/volume ratio. This solution was added dropwise into a 3 L glass reactor containing a mixture of deionized H_2O and NH_3 gas at 70 °C. The suspension formed was filtered in vacuo and washed twice with a H_2O/NH_3 mixture. The washed powder was dried at 110 °C for 12 h and calcined at 500 °C for 4 h under air at 5 °C/min.

MAH and MgO

MAH was prepared by the co-precipitation method. First, $MgSO_4$ and $Al_2(SO_4)_3$ were dissolved in deionized H_2O (200 mL) with an Mg/(Mg+Al) ratio of 0.75. The resulting solution was added dropwise, under constant stirring at 60 °C, into a 3-L glass reactor containing aq 0.5 M Na_2CO_3 (500 mL) and the pH was adjusted to 11. Subsequently, the temperature was increased to 80 °C and stirring continued for 18 h. The solid formed was filtered in vacuo, washed with H_2O, and then dried at 80 °C for 2 h at 3 °C/min. MgO was prepared in a similar procedure.

Imines and Iminoesters 5; General Procedure

In a 25 mL round-bottomed flask were mixed the corresponding aniline (4.0 mmol), aldehyde (4.4 mmol, 1.1 equiv), and MeOH (ca. 3.0 mL). The reaction mixture was irradiated by microwave energy in an open vessel (150 W) at 60 °C for 30 min. The reaction progress was monitored by TLC. Upon completion, the mixture was cooled to r.t. and MeOH was removed under reduced pressure. The pure product was precipitated with a DCM/hexane mixture (5:95).

***N*-Benzylidenaniline (5a)**

Yellow solid; yield: 1.088 g (93%); mp 51–52 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.28 (1 H, s, HC=N), 7.82–7.80 (2 H, m, H-8, H-12), 7.33–7.29 (5 H, m, H-2, H-6, H-9, H-10, H-11), 7.27–7.13 (3 H, m, H-3, H-4, H-5).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.5 (C=N), 152.2 (C-1), 136.4 (C-7), 131.6 (C-10), 129.4 (C-8, C-12), 129.1 (C-3, C-5), 129.0 (C-9, C-11), 126.2 (C-4), 121.2 (C-2, C-6).

Spectral data are consistent with the literature.[51]

***N*-(4-Methoxybenzylidene)aniline (5b)**

White solid; yield: 1.224 g (90%); mp 61–62 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.35 (1 H, s, HC=N), 7.84 (2 H, d, *J* = 8.8 Hz, H-8, H-12), 7.37 (2 H, t, *J* = 7.9 Hz, H-2, H-6), 7.20–7.15 (3 H, m, H-3, H-4, H-5), 6.95 (2 H, d, *J* = 8.8 Hz, H-9, H-11), 3.82 (3 H, s, OCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.3 (C-10), 159.7 (C=N), 152.4 (C-1), 130.6 (C-8, C-12), 129.3 (C-3, C-5), 129.2 (C-7), 125.6 (C-4), 120.9 (C-2, C-6), 114.2 (C-9, C-11), 55.4 (OCH_3).

Spectral data are consistent with the literature.[51]

***N*-(4-Nitrobenzylidene)aniline (5c)**

Orange oil; yield: 1.226 g (84%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.51 (1 H, s, HC=N), 8.26 (2 H, d, *J* = 8.6 Hz, H-9, H-11), 8.03 (2 H, d, *J* = 8.6 Hz, H-8, H-12), 7.46–7.35 (2 H, m, H-2, H-6), 7.31–7.18 (3 H, m, H-3, H-4, H-5).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.4 (C=N), 150.9 (C-10), 149.3 (C-1), 141.6 (C-7), 129.4 (C-8, C-12), 129.4 (C-3, C-5), 127.1 (C-4), 124.0 (C-9, C-11), 121.1 (C-2, C-6).

Spectral data are consistent with the literature.[52]

***N*-(4-Fluorobenzylidene)aniline (5d)**

Beige solid; yield: 1.114 g (87%); mp 45–46 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.32 (1 H, s, HC=N), 7.83 (2 H, m, H-8, H-12), 7.38–7.31 (2 H, m, H-2, H-6), 7.21–7.14 (3 H, m, H-3, H-4, H-5), 7.11–7.06 (2 H, m, H-9, H-11).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.8 (*J* = 252.1 Hz, C-10), 158.8 (C=N), 151.9 (C-1), 132.7 (*J* = 3.0 Hz, C-7), 130.9 (*J* = 8.8 Hz, C-8, C-12), 129.3 (C-3, C-5), 126.1 (C-4), 121.0 (C-2, C-6), 115.9 (*J* = 22.0 Hz, C-9, C-11).

Spectral data are consistent with the literature.[52]

***N*-(Benzylidene)-4-nitroaniline (5e)**

Golden solid; yield: 1.285 g (88%); mp 79–80 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.51 (1 H, s, HC=N), 8.26 (2 H, d, *J* = 8.6 Hz, H-3, H-5), 8.03 (2 H, d, *J* = 8.6 Hz, H-2, H-6), 7.42–7.39 (2 H, m, H-8, H-12), 7.29–7.24 (3 H, m, H-9, H-10, H-11).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.4 (C=N), 150.9 (C-4), 149.3 (C-7), 141.6 (C-1), 129.4 (C-2, C-6), 129.4 (C-9, C-11), 127.1 (C-10), 124.0 (C-3, C-5), 121.1 (C-8, C-12).

***N*-(Benzylidene)-4-bromoaniline (5f)**

Silver solid; yield: 1.529 g (91%); mp 65–66 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.42 (1 H, s, HC=N), 7.93 (2 H, d, *J* = 7.5 Hz, H-3, H-5), 7.54–7.46 (5 H, m, H-8, H-9, H-10, H-11, H-12), 7.13 (2 H, d, *J* = 5.5 Hz, H-2, H-6).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.7 (C=N), 160.0 (C-1), 136.1 (C-7), 132.3 (C-3, C-5), 131.8 (C-10), 129.1 (C-8, C-12), 129.0 (C-9, C-11), 122.8 (C-2, C-6), 119.5 (C-4).

Spectral data are consistent with the literature.[53]

***N*-(3-Chlorobenzylidene)-4-chloroaniline (5g)**

Green liquid; yield: 1.050 g (89%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.31 (1 H, s, HC=N), 7.86 (1 H, s, H-8), 7.54 (1 H, ddd, *J* = 8.0, 2.1, 1.1 Hz, H-12), 7.44–7.38 (3 H, m, H-3, H-5, H-10), 7.38–7.29 (3 H, m, H-2, H-6, H-11).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.9 (C=N), 149.8 (C-1), 137.8 (C-7), 135.3 (C-9), 134.9 (C-10), 134.3 (C-4), 130.4 (C-11), 129.3 (C-3, C-5), 129.1 (C-8), 128.0 (C-12), 122.3 (C-2, C-6).

***N*-(Thiophen-2-ylmethylene)-4-chloroaniline (5h)**

Brown solid; yield: 821.6 mg (79%); mp 72–73 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.49 (1 H, s, HC=N), 7.48 (1 H, d, *J* = 4.8 Hz, H-9), 7.45 (1 H, d, *J* = 3.0 Hz, H-11), 7.30 (2 H, d, *J* = 8.4 Hz, H-3, H-5), 7.18–7.07 (3 H, m, H-2, H-6, H-10).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.3 (C=N), 149.9 (C-1), 142.6 (C-7), 132.7 (C-8), 131.5 (C-4), 130.8 (C-10), 129.3 (C-3, C-5), 127.9 (C-9), 122.4 (C-2, C-6).

Spectral data are consistent with the literature.[51]

***N*-(Furan-2-ylmethylene)-4-chloroaniline (5i)**

Black oil; yield: 735.0 mg (76%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.26 (1 H, s, HC=N), 7.62 (1 H, d, *J* = 1.7 Hz, H-9), 7.34 (2 H, d, *J* = 8.8 Hz, H-3, H-5), 7.17 (2 H, d, *J* = 8.7 Hz, H-2, H-6), 6.98 (1 H, d, *J* = 3.0 Hz, H-8), 6.57 (1 H, dd, *J* = 3.5, 1.8 Hz, H-9).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.9 (C-1), 149.8 (C-7), 148.0 (C=N), (C-7), 146.0 (C-9), 131.8 (C-4), 129.3 (C-3, C-5), 122.3 (C-2, C-6), 116.9 (C-11), 112.3 (C-10).

Spectral data are consistent with the literature.[54]

***N*-(4-Nitrobenzylidene)-4-methoxyaniline (5j)**

Golden solid; yield: 1.175 g (94%); mp 131–132 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.57 (1 H, s, HC=N), 8.30 (2 H, d, *J* = 8.3 Hz, H-9, H-11), 8.04 (2 H, d, *J* = 8.3 Hz, H-8, H-12), 7.30 (2 H, d, *J* = 8.4 Hz, H-2, H-6), 6.96 (2 H, d, *J* = 8.4 Hz, H-3, H-5), 3.85 (3 H, s, OCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.3 (C-4), 154.8 (C=N), 149.0 (C-10), 143.6 (C-1), 142.0 (C-7), 129.1 (C-8, C-12), 124.0 (C-9, C-11), 122.6 (C-2, C-6), 114.6 (C-3, C-5), 55.5 (OCH_3).

Spectral data are consistent with the literature.[52,53]

***N*-(4-Methoxybenzylidene)-4-methoxyaniline (5k)**

Olive green solid; yield: 1.049 g (89%); mp 145–146 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.39 (1 H, s, HC=N), 7.82 (2 H, d, *J* = 4.9 Hz, H-8, H-12), 7.20 (2 H, d, *J* = 4.8 Hz, H-2, H-6), 6.94 (2 H, d, *J* = 5.5 Hz, H-3, H-5), 3.84 (3 H, s, OCH_3), 3.81 (3 H, s, OCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.0 (C=N), 158.0 (C-10), 145.2 (C-4), 130.3 (C-8, C-12), 129.5 (C-1), 122.1 (C-2, C-6), 114.4 (C-3, C-5), 114.2 (C-9, C-11), 55.5 (OCH_3), 55.5 (OCH_3).

Spectral data are consistent with the literature.[52,53]

***N*-(4-Methoxybenzylidene)-4-chloroaniline (5l)**

Beige solid; yield: 881.6 mg (76%); mp 89–90 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.29 (1 H, s, HC=N), 7.79 (2 H, d, *J* = 8.8 Hz, H-8, H-12), 7.29 (2 H, d, *J* = 8.6 Hz, H-3, H-5), 7.09 (2 H, d, *J* = 8.6 Hz, H-2, H-6), 6.98–6.89 (2 H, m, H-9, H-11), 3.81 (3 H, s, OCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.5 (C-10), 160.0 (C=N), 150.8 (C-1), 132.0 (C-4), 131.0 (C-8, C-12), 130.7 (C-3, C-5), 129.2 (C-7), 122.8 (C-2, C-6), 114.3 (C-9, C-11), 55.4 (OCH_3).

Spectral data are consistent with the literature.[55]

N-(2,4-Dichlorobenzylidene)-4-chloroaniline (5n)

White solid; yield: 1.112 g (83%); mp 127–128 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.82 (1 H, s, HC=N), 8.18 (1 H, d, *J* = 8.4 Hz, H-12), 7.45 (1 H, s, H-9), 7.36 (3 H, m, H-11, H-2, H-6), 7.18 (2 H, d, *J* = 7.7 Hz, H-5, H-4).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.0 (C=N), 150.0 (C-1), 138.0 (C-4), 136.7 (C-7), 132.4 (C-12), 131.7 (C-10), 129.9 (C-11), 129.6 (C-8), 129.5 (C-3, C-5), 127.9 (C-9), 122.6 (C-2, C-6).

N-[(*E*)-Cinnamylidene]-4-methoxyaniline (5o)

Silver solid; yield: 904.8 mg (78%); mp 119–120 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.34–8.23 (1 H, m, HC=N), 7.52 (2 H, d, *J* = 7.3 Hz, H-8, H-12), 7.37 (2 H, t, *J* = 7.3 Hz, H-9, H-11), 7.33 (1 H, d, *J* = 7.1 Hz, H-14), 7.20 (2 H, d, *J* = 8.7 Hz, H-2, H-6), 7.09 (2 H, s, H-10, H-13), 6.91 (2 H, d, *J* = 8.7 Hz, H-3, H-5), 3.80 (3 H, s, OCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.5 (C=N), 158.4 (C-4), 144.6 (C-1), 143.1 (C-13), 135.8 (C-7), 129.4 (C-10), 128.9 (C-14), 128.8 (C-9, C-11), 127.4 (C-8, C-12), 122.3 (C-2, C-6), 114.5 (C-3, C-5), 55.5 (OCH_3).

Spectral data are consistent with the literature.[53]

Methyl *N*-[(4-Fluorobenzylidene)amino]acetate (5p)

Amber oil; yield: 1.297 g (99%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.25 (1 H, s, H-1′), 7.78–7.75 (2 H, m, H-3′), 7.13–7.06 (2 H, td, *J* = 8.6, 1.7 Hz, H-4′), 4.40 (2 H, s, H-2), 3.77 (3 H, s, CO_2CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.5 (C-1), 166.3 (*J* = 249.7 Hz, C-5′), 163.9 (C-1′), 132.1 (C-2′), 130.5 (*J* = 8.2 Hz, C-3′), 115.7 (*J* = 21.7 Hz, C-4′), 61.7 (C-2), 52.1 (CO_2CH_3).

Methyl *N*-[(4-Fluorobenzylidene)amino]hexanoate (5q)

White oil; yield: 778.6 mg (86%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.98 (1 H, s, H-1′), 7.94–7.91 (2 H, m, H-3′), 7.24–7.21 (2 H, m, H-4′), 3.66 (3 H, s, CO_2CH_3), 3.65 (2 H, s, H-6), 2.34 (2 H, t, *J* = 7.4 Hz, H-2), 1.84 (2 H, dt, *J* = 15.4, 7.7 Hz, H-3), 1.66 (2 H, dt, *J* = 15.2, 7.5 Hz, H-5), 1.45 (2 H, dt, *J* = 15.4, 7.8 Hz, H-4).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.5 (C-1), 173.9 (C-1′), 166.5 (*J* = 256.6 Hz, C-5′), 132.9 (*J* = 2.7 Hz, C-2′), 132.2 (*J* = 9.7 Hz, C-3′), 116.3 (*J* = 22.3 Hz, C-4′), 51.5 (CO_2CH_3), 39.7 (C-6), 33.6 (C-2), 27.1 (C-5), 25.9 (C-4), 24.2 (C-3).

3-Chloroazetidin-2-ones 7a–s and 8b–o; General Procedure

The imine **5** (2 mmol), the solid catalyst (5% w/w), DMF (21.0 mmol, 10.5 equiv, ca. 1.8 mL), and acyl chloride **6** (2.4 mmol, 1.2 equiv) were placed in a 25 mL round-bottomed flask under N_2 atmosphere. The mixture was stirred at r.t. for 5 min and then irradiated by microwaves (300 W) in an open vessel at 180 °C for 2 min. The reaction progress was monitored by TLC and GC-MS. Upon completion of the reaction, the crude was extracted with DCM (3 × 10 mL) and the combined organic extracts were washed with H_2O, and dried (Na_2SO_4). After removing DCM under reduced pressure, the crude mixture was purified by column chromatography over 230–400 mesh SiO_2 and EtOAc/hexane (5:95) as eluent.

For catalyst recycling, the reaction mixture was filtered in vacuo before extraction and washed with DCM. For catalyst reactivation, it was additionally washed with H_2O and stove-dried at 120 °C for 10 min.

cis-3-Chloro-1,4-diphenylazetidin-2-one (7a)

Orange crystals; yield: 284.4 mg (40%); mp 179–180 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41–7.35 (5 H, m, H-2′, H-3′, H-4′), 7.33-7.30 (3 H, m, H-2, H-4), 7.29–7.25 (2 H, m, H-3), 5.41 (1 H, d, *J* = 5.3 Hz, H_a), 5.26 (1 H, d, *J* = 5.4 Hz, H_b).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.2 (C=O), 136.8 (C-1), 132.7 (C-1′), 129.2 (C-3′), 128.7 (C-2′), 127.8 (C-3), 124.9 (C-4′), 120.2 (C-4), 117.6 (C-2), 60.8 (C_b), 60.5 (C_a).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $[C_{15}H_{13}ClNO]^+$: 258.0685; found: 258.0681.

trans-3-Chloro-1,4-diphenylazetidin-2-one (7a′)

Red oil; yield: 369.7 mg (52%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38–7.34 (5 H, m, H-2′, H-3′, H-4′), 7.29–7.27 (3 H, m, H-2, H-4), 7.26–7.21 (2 H, m, H-3), 5.00 (1 H, d, *J* = 1.9 Hz, H_a), 4.58 (1 H, d, *J* = 1.9 Hz, H_b).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.7 (C=O), 136.9 (C-1), 135.0 (C-1′), 129.5 (C-3′), 127.5 (C-2′), 126.2 (C-3), 124.9 (C-4′), 124.8 (C-4), 114.9 (C-2), 66.1 (C_b), 63.3 (C_a).

cis-3-Chloro-4-(4-methoxyphenyl)-1-phenylazetidin-2-one (7b)

Yellow crystals; yield: 245.2 mg (36%); mp 173–174 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 (2 H, dd, *J* = 8.6, 1.1 Hz, H-2′), 7.27 (2 H, dd, *J* = 15.0, 2.8 Hz, H-2), 7.24 (2 H, d, *J* = 8.7 Hz, H-3), 7.13–7.07 (1 H, m, H-4), 6.93 (2 H, d, *J* = 8.7 Hz, H-3′), 5.37 (1 H, d, *J* = 5.3 Hz, H_a), 5.24 (1 H, d, *J* = 5.3 Hz, H_b), 3.81 (3 H, s, OCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.4 (C=O), 160.2 (C-4′), 136.8 (C-1), 130.7 (C-2′), 124.8 (C-4), 124.4 (C-1′), 120.1 (C-3), 117.6 (C-2), 114.1 (C-3′), 60.8 (C_b), 60.5 (C_a), 55.3 (OCH_3).

trans-3-Chloro-4-(4-methoxyphenyl)-1-phenyazetidin-2-one (7b′)

Yellow solid; yield: 360.9 mg (53%); mp 89–90 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 (4 H, d, *J* = 8.7 Hz, H-2′, H-2), 7.26–723 (2 H, m, H-3), 7.09–7.06 (1 H, m, H-4), 6.91 (2 H, d, *J* = 8.7 Hz, H-3′), 4.96 (1 H, d, *J* = 1.9 Hz, H_a), 4.58 (1 H, d, *J* = 1.9 Hz, H_b), 3.79 (3 H, s, OCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.9 (C=O), 160.5 (C-4′), 136.9 (C-1), 129.2 (C-2′), 127.5 (C-3), 124.8 (C-4), 120.3 (C-1′), 117.6 (C-2), 114.9 (C-3′), 65.8 (C_b), 63.3 (C_a), 55.4 (OCH_3).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $[C_{16}H_{15}ClNO_2]^+$: 288.7508; found: 288.0778.

cis-3-Chloro-4-(4-nitrophenyl)-1-phenylazetidin-2-one (7c)

Red solid; yield: 314.4 mg (47%); mp 152–153 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.26 (2 H, d, *J* = 8.7 Hz, H-3′), 7.50 (2 H, d, *J* = 8.6 Hz, H-2′), 7.33–7.25 (4 H, m, H-2, H-3), 7.18–7.11 (1 H, m, H-4), 5.55 (1 H, d, *J* = 5.4 Hz, H_a), 5.36 (1 H, d, *J* = 5.4 Hz, H_b).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.5 (C=O), 148.5 (C-4′), 140.2 (C-1′), 136.2 (C-1), 129.5 (C-2), 128.8 (C-2′), 125.4 (C-4), 124.0 (C-3′), 117.3 (C-3), 60.2 (C_b), 59.9 (C_a).

***trans*-3-Chloro-4-(4-nitrophenyl)-1-phenylazetidin-2-one (7c′)**

Red oil; yield: 254.2 mg (38%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.29–8.27 (2 H, m, H-3′), 7.59–7.58 (2 H, m, H-2′), 7.57–7.30 (2 H, m, H-2), 7.28–7.25 (2 H, m, H-3), 7.23–7.14 (1 H, m, H-4), 5.14 (1 H, d, *J* = 1.9 Hz, H_a), 4.63 (1 H, d, *J* = 2.0 Hz, H_b).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.9 (C=O), 148.6 (C-4′), 142.0 (C-1′), 136.3 (C-1), 129.5 (C-2), 127.1 (C-2′), 125.4 (C-4), 124.8 (C-3′), 117.4 (C-3), 64.9 (C_b), 63.0 (C_a).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for [$C_{15}H_{12}ClN_2O_3$]$^+$: 303.0536; found: 303.0530.

***cis*-3-Chloro-4-(4-fluorophenyl)-1-phenylazetidin-2-one (7d)**

White solid; yield: 269.9 mg (39%); mp 174–175 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31–7.25 (6 H, m, H-2′, H-2, H-3), 7.13–7.07 (3 H, m, H-3′, H-4), 5.41 (1 H, d, *J* = 5.3 Hz, H_a), 5.26 (1 H, d, *J* = 5.3 Hz, H_b).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.2 (*J* = 248.4 Hz, C-4′), 161.1 (C=O), 136.6 (C-1), 129.6 (*J* = 8.4 Hz, C-2′), 129.3 (C-3), 128.5 (*J* = 2.8 Hz, C-1′), 125.0 (C-4), 117.5 (C-2), 115.8 (*J* = 21.9 Hz, C-3′), 60.5 (C_b), 60.2 (C_a).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for [$C_{15}H_{12}ClFNO$]$^+$: 276.0591; found: 276.0554.

***trans*-3-Chloro-4-(4-fluorophenyl)-1-phenylazetidin-2-one (7d′)**

Yellow solid; yield: 373.6 mg (54%); mp 117–118 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.33 (2 H, m, H-2′), 7.29–7.22 (4 H, m, H-2, H-3), 7.12–7.05 (3 H, m, H-3′, H-4), 5.01 (1 H, d, *J* = 1.8 Hz, H_a), 4.58 (1 H, d, *J* = 1.9 Hz, H_b).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.3 (*J* = 249.0 Hz, C-4′), 160.6 (C=O), 136.7 (C-1), 130.9 (*J* = 3.2 Hz, C-1′), 129.3 (C-3), 128.1 (*J* = 8.4 Hz, C-2′), 125.0 (C-4), 117.6 (C-2), 116.6 (*J* = 21.9 Hz, C-3′), 65.3 (C_b), 63.2 (C_a).

***cis*-3-Chloro-1-(4-nitrophenyl)-4-phenylazetidin-2-one (7e)**

Red solid; yield: 194.0 mg (29%); mp 140–142 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.26 (2 H, d, *J* = 8.7 Hz, H-3), 7.50 (2 H, d, *J* = 8.6 Hz, H-3′), 7.33–7.25 (4 H, m, H-2′, H-2), 7.18–7.11 (1 H, m, H-4′), 5.55 (1 H, d, *J* = 5.4 Hz, H_a), 5.36 (1 H, d, *J* = 5.4 Hz, H_b).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.5 (C=O), 148.5 (C-4), 140.2 (C-1′), 136.2 (C-1), 129.5 (C-4′), 128.8 (C-3′), 125.4 (C-2), 124.0 (C-2′), 117.3 (C-3), 60.2 (C_b), 59.9 (C_a).

***trans*-3-Chloro-1-(4-nitrophenyl)-4-phenylazetidin-2-one (7e′)**

Red solid; yield: 194.0 mg (29%); mp 140–142 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.16 (2 H, d, *J* = 9.1 Hz, H-3), 7.49–7.34 (7 H, m, H-2′, H-3′, H-4′, H-2), 5.10 (1 H, d, *J* = 2.0 Hz, H_a), 4.71 (1 H, d, *J* = 2.1 Hz, H_b).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.3 (C=O), 144.1 (C-4), 141.8 (C-1), 133.9 (C-1′), 130.1 (C-4′), 129.8 (C-3′), 125.9 (C-2), 125.3 (C-2′), 117.5 (C-3), 66.7 (C_b), 63.5 (C_a).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for [$C_{15}H_{12}ClN_2O_3$]$^+$: 303.0536; found: 303.0497.

***cis*-3-Chloro-1-(4-bromophenyl)-4-phenylazetidin-2-one (7f)**

Yellow solid; yield: 161.8 mg (25%); mp 179–180 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42–7.38 (5 H, m, H-3′, H-4′, H-3), 7.29–7.26 (2 H, m, H-2′), 7.20 (2 H, d, *J* = 8.8 Hz, H-2), 5.40 (1 H, d, *J* = 5.3 Hz, H_a), 5.28 (1 H, d, *J* = 5.3 Hz, H_b).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.1 (C=O), 135.7 (C-1), 132.3 (C-3), 132.1 (C-1′), 129.4 (C-4′), 128.8 (C-3′), 127.8 (C-2′), 119.1 (C-2), 117.8 (C-4), 60.9 (C_b), 60.6 (C_a).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for [$C_{15}H_{12}BrClNO$]$^+$: 335.9791; found: 335.9758.

***trans*-3-Chloro-1-(4-bromophenyl)-4-phenylazetidin-2-one (7f′)**

Red solid; yield: 213.5 mg (33%); mp 140–142 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.38 (3 H, m, H-4′, H-3), 7.35–7.33 (4 H, m, H-2′, H-3′), 7.32–7.14 (2 H, m, H-2), 4.99 (1 H, d, *J* = 2.0 Hz, H_a), 4.60 (1 H, d, *J* = 2.0 Hz, H_b).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.7 (C=O), 135.8 (C-1), 134.5 (C-1′), 132.3 (C-3), 129.7 (C-4′), 129.6 (C-3′), 126.1 (C-2′), 119.1 (C-2), 117.8 (C-4), 66.2 (C_b), 63.4 (C_a).

***cis*-3-Chloro-1-(4-chlorophenyl)-4-(3-chlorophenyl)azetidin-2-one (7g)**

White crystals; yield: 359.0 mg (55%); mp 177–178 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.33 (2 H, m, H-3), 7.29–7.23 (4 H, m, H-5′, H-2′, H-2), 7.17 (1 H, d, *J* = 7.4 Hz, H-6′), 5.37 (1 H, d, *J* = 5.3 Hz, H_a), 5.28 (1 H, d, *J* = 5.4 Hz, H_b).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.8 (C=O), 135.0 (C-1′), 134.9 (C-1), 134.4 (C-3′), 130.3 (C-6′), 130.2 (C-4), 129.7 (C-2′), 129.5 (C-3), 127.9 (C-5′), 125.9 (C-4′), 118.6 (C-2), 60.5 (C_b), 60.3 (C_a).

***trans*-3-Chloro-1-(4-chlorophenyl)-4-(3-chlorophenyl)azetidin-2-one (7g′)**

Dark yellow liquid; yield: 208.9 mg (32%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.40–7.35 (3 H, m, H-2′, H-3), 7.26–7.20 (5 H, m, H-6′, H-5′, H-4′, H-2), 4.96 (1 H, d, *J* = 1.9 Hz, H_a), 4.62 (1 H, d, *J* = 2.0 Hz, H_b).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.3 (C=O), 136.7 (C-1′), 135.7 (C-1), 135.0 (C-3′), 131.0 (C-6′), 130.4 (C-4), 130.0 (C-2′), 129.5 (C-3), 126.3 (C-5′), 124.1 (C-4′), 118.7 (C-2), 65.5 (C_b), 63.3 (C_a).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for [$C_{15}H_{11}Cl_3NO$]$^+$: 325.9906; found: 325.9878.

***cis*-3-Chloro-1-(4-chlorophenyl)-4-(2-thiophen-2-yl)azetidin-2-one (7h)**

Yellow solid, yield: 147.9 mg (22%); mp 71–72 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.39 (1 H, dd, *J* = 5.0, 1.2 Hz, H-3′), 7.32–7.27 (2 H, m, H-3), 7.27–7.22 (2 H, m, H-2), 7.12–7.09 (1 H, m, H-4′), 7.06 (1 H, dd, *J* = 5.0, 3.6 Hz, H-5′), 5.65 (1 H, d, *J* = 5.2 Hz, H_a), 5.28 (1 H, d, *J* = 5.2 Hz, H_b).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.9 (C=O), 135.3 (C-1′), 135.1 (C-1), 130.2 (C-4), 129.4 (C-3), 128.2 (C-3′), 127.4 (C-4′), 127.1 (C-5′), 118.7 (C-2), 61.2 (C_b), 57.3 (C_a).

***trans*-3-Chloro-1-(4-chlorophenyl)-4-(2-thiophen-2-yl)azetidin-2-one (7h′)**

Dark yellow solid, yield: 147.9 mg (22%); mp 95–96 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.50 (1 H, d, *J* = 3.4 Hz, H-3′), 7.34–7.29 (2 H, m, H-3), 7.28–7.23 (2 H, m, H-2), 7.19 (1 H, d, *J* = 3.2 Hz, H-4′), 7.15 (1 H, dd, *J* = 5.0, 3.8 Hz, H-5′), 5.26 (1 H, d, *J* = 1.8 Hz, H_a), 4.74 (1 H, d, *J* = 1.9 Hz, H_b).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.9 (C=O), 136.6 (C-1′), 135.9 (C-1), 131.2 (C-4), 129.4 (C-3′), 129.2 (C-3), 128.9 (C-4′), 127.3 (C-5′), 121.5 (C-2), 64.0 (C_b), 62.0 (C_a).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $[C_{13}H_{10}Cl_2NOS]^+$: 297.9860; found: 297.9837.

cis-3-Chloro-1-(4-methoxyphenyl)-4-(4-nitrophenyl)azetidin-2-one (7j)

Red crystals; yield: 357.1 mg (55%); mp 136–137 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.25 (2 H, d, *J* = 8.4 Hz, H-3′), 7.49 (2 H, d, *J* = 8.6 Hz, H-2′), 7.22 (2 H, d, *J* = 9.0 Hz, H-2), 6.82 (2 H, d, *J* = 9.0 Hz, H-3), 5.53 (1 H, d, *J* = 4.9 Hz, H_a), 5.35 (1 H, d, *J* = 5.2 Hz, H_b), 3.75 (3 H, s, OCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.0 (C=O), 157.0 (C-4), 148.4 (C-1′), 140.4 (C-4′), 129.7 (C-1), 128.9 (C-2′), 123.9 (C-3′), 118.7 (C-2), 114.7 (C-3), 60.3 (C_b), 60.0 (C_a), 55.5 (OCH_3).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $[C_{16}H_{13}ClN_2O_4]^+$: 332.0564; found: 332.0825.

trans-3-Chloro-1-(4-methoxyphenyl)-4-(4-nitrophenyl)azetidin-2-one (7j′)

Yellow crystals; yield: 259.7 mg (40%); mp 139–140 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.26 (2 H, d, *J* = 8.7 Hz, H-3′), 7.58 (2 H, d, *J* = 8.7 Hz, H-2′), 7.19 (2 H, d, *J* = 9.0 Hz, H-2), 6.81 (2 H, d, *J* = 9.0 Hz, H-3), 5.12 (1 H, d, *J* = 1.6 Hz, H_a), 4.64 (1 H, d, *J* = 1.8 Hz, H_b), 3.75 (3 H, s, OCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.4 (C=O), 157.1 (C-4), 148.6 (C-1′), 142.2 (C-4′), 129.6 (C-1), 127.3 (C-2′), 124.7 (C-3′), 118.9 (C-2), 114.7 (C-3), 65.0 (C_b), 63.0 (C_a), 55.5 (OCH_3).

cis-3-Chloro-1-(4-methoxyphenyl)-4-(4-methoxyphenyl)azetidin-2-one (7k)

White solid; yield: 302.9 mg (46%); mp 165–166 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26 (2 H, d, *J* = 9.1 Hz, H-2′), 7.22 (2 H, d, *J* = 8.7 Hz, H-2), 6.92 (2 H, d, *J* = 8.7 Hz, H-3), 6.79 (2 H, d, *J* = 9.1 Hz, H-3′), 5.32 (1 H, d, *J* = 5.2 Hz, H_a), 5.22 (1 H, d, *J* = 5.2 Hz, H_b), 3.81 (3 H, s, C_4-OCH_3), 3.74 (3 H, s, C_4′-OCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.8 (C=O), 160.2 (C-4′), 156.7 (C-4), 130.3 (C-1′), 129.2 (C-2′), 124.5 (C-1), 118.9 (C-2), 114.4 (C-3), 114.1 (C-3′), 60.9 (C_b), 60.6 (C_a), 55.4 (C_4-OCH_3), 55.3 (C_4′-OCH_3).

trans-3-Chloro-1-(4-methoxyphenyl)-4-(4-methoxyphenyl)azetidin-2-one (7k′)

White crystals; yield: 204.1 mg (31%); mp 112–113 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26 (2 H, d, *J* = 8.7 Hz, H-2′), 7.22 (2 H, d, *J* = 9.1 Hz, H-2), 6.90 (2 H, d, *J* = 8.7 Hz, H-3′), 6.76 (2 H, d, *J* = 9.1 Hz, H-3), 4.90 (1 H, d, *J* = 1.7 Hz, H_a), 4.55 (1 H, d, *J* = 1.9 Hz, H_b), 3.78 (3 H, s, C4-OCH_3), 3.71 (3 H, s, C4′-OCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.5 (C=O), 160.2 (C-4′), 156.7 (C-4), 130.3 (C-1′), 127.5 (C-2′), 126.9 (C-1), 118.9 (C-2), 114.8 (C-3), 114.4 (C-3′), 65.9 (C_b), 63.4 (C_a), 55.3 (C_4-OCH_3), 55.2 (C_4′-OCH_3).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $[C_{17}H_{17}ClNO_3]^+$: 318.0897; found: 318.1517.

cis-3-Chloro-1-(4-chlorophenyl)-4-(4-methoxyphenyl)azetidin-2-one (7l)

White solid; yield: 301.5 mg (46%); mp 180–181 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.24–7.09 (6 H, m, H-2′, H-2, H-3), 6.85 (2 H, d, *J* = 8.4 Hz, H-3′), 5.28 (1 H, d, *J* = 5.1 Hz, H_a), 5.17 (1 H, d, *J* = 5.2 Hz, H_b), 3.74 (3 H, s, OCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.3 (C=O), 160.4 (C-4′), 135.3 (C-1), 130.0 (C-4), 129.3 (C-2′), 129.2 (C-3), 123.9 (C-1′), 118.8 (C-2), 114.2 (C-3′), 60.9 (C_b), 60.7 (C_a), 55.3 (OCH_3).

trans-3-Chloro-1-(4-chlorophenyl)-4-(4-methoxyphenyl)azetidin-2-one (7l′)

White solid; yield: 262.2 mg (40%); mp 164–165 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27 (2 H, d, *J* = 8.7 Hz, H-2), 7.23–7.18 (4 H, m, H-2′, H-3), 6.93 (2 H, d, *J* = 8.7 Hz, H-3′), 4.95 (1 H, d, *J* = 1.9 Hz, H_a), 4.60 (1 H, d, *J* = 1.9 Hz, H_b), 3.81 (3 H, s, OCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.8 (C=O), 160.6 (C-4′), 135.3 (C-1), 130.0 (C-4), 129.3 (C-2′), 127.5 (C-3), 126.3 (C-1′), 118.8 (C-2), 114.9 (C-3′), 66.0 (C_b), 63.4 (C_a), 55.4 (OCH_3).

HRMS (ESI+): *m*/*z* [M + Na]$^+$ calcd for $[C_{16}H_{13}Cl_{l2}NO_2Na]^+$: 344.0221; found: 344.0289.

cis-3-Bromo-1-(4-methoxyphenyl)-4-(4-nitrophenyl)azetidin-2-one (7m)

Brown solid; yield: 404.8 mg (55%); mp 129–130 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.25 (2 H, d, *J* = 8.4 Hz, H-3′), 7.49 (2 H, d, *J* = 8.6 Hz, H-2′), 7.22 (2 H, d, *J* = 9.0 Hz, H-2), 6.82 (2 H, d, *J* = 9.0 Hz, H-3), 5.53 (1 H, d, *J* = 4.9 Hz, H_a), 5.35 (1 H, d, *J* = 5.2 Hz, H_b), 3.75 (3 H, s, OCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.0 (C=O), 157.0 (C-4), 148.4 (C-1′), 140.4 (C-4′), 129.7 (C-1), 128.9 (C-2′), 123.9 (C-3′), 118.7 (C-2), 114.7 (C-3), 60.3 (C_b), 60.0 (C_a), 55.5 (OCH_3).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $[C_{16}H_{14}BrN_2O_4]^+$: 377.0137; found: 377.0095.

cis-3-Chloro-*N*-(4-chlorophenyl)-4-(2,4-dichlorobenzyl)azetidin-2-one (7n)

White crystals; yield: 266.4 mg (42%); mp 151–152 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52 (1 H, s, H-3′), 7.27 (5 H, m, H-5′, H-3, H-2), 7.07 (1 H, d, *J* = 8.4 Hz, H-6′), 5.73 (1 H, d, *J* = 5.2 Hz, H_a), 5.38 (1 H, d, *J* = 5.2 Hz, H_b).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.8 (C=O), 135.8 (C-1′), 135.0 (C-1), 134.4 (C-4′), 130.6 (C-3′), 130.0 (C-4), 129.7 (C-2′), 129.3(C-3), 129.1 (C-5′), 127.6 (C-2), 118.7 (C-6′), 60.2 (C_b), 58.1 (C_a).

trans-3-Chloro-1-(4-chlorophenyl)-4-(2,4-dichlorophenyl)azetidin-2-one (7n′)

White crystals; yield: 272.8 mg (43%); mp 131–132 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52 (1 H, s, H-3′), 7.24 (5 H, m, H-5′, H-3, H-2), 7.11 (1 H, d, *J* = 8.4 Hz, H-6′), 5.73 (1 H, s, H_a), 5.38 (1 H, s, H_b).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.4 (C=O), 136.0(C-1′), 135.1 (C-1), 134.2(C-4′), 130.9 (C-3′), 130.6 (C-4), 130.5 (C-2′), 129.7 (C-3), 128.2 (C-5′), 127.8 (C-2), 118.8 (C-6′), 62.7 (C_b), 62.3 (C_a).

cis-3-Chloro-1-(4-methoxyphenyl)-4-[(*E*)-styryl]azetidin-2-one (7o)

Brown solid; yield: 171.9 mg (26%); mp 122–123 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (2 H, dd, *J* = 16.5, 8.1 Hz, H-2), 7.35 (2 H, t, *J* = 7.3 Hz, H-5′), 7.31 (2 H, d, *J* = 7.2 Hz, H-4′), 6.88–6.81 (2 H, m, H-2′, H-6′), 6.86–6.82 (2 H, m, H-3), 6.29 (1 H, dd, *J* = 15.9, 8.5 Hz, H-1′), 5.17 (1 H, d, *J* = 5.2 Hz, H_a), 4.92 (1 H, dd, *J* = 8.4, 5.2 Hz, H_b), 3.76 (3 H, s, OCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.4 (C=O), 156.8 (C-4), 137.5 (C-2′), 135.5 (C-3′), 130.8 (C-1), 128.8 (C-4′, C-6′), 126.9 (C-5′), 123.1 (C-1′), 118.8 (C-2), 114.5 (C-3), 60.3 (C_b), 59.8 (C_a), 55.5 (OCH_3).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $[C_{18}H_{17}ClNO_2]^+$: 314.0948; found: 314.0910.

trans-3-Chloro-1-(4-methoxyphenyl)-4-[(*E*)-styryl]azetidin-2-one (7o′)

White crystals; yield: 211.6 mg (32%); mp 120–121 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.38 (4 H, m, H-5′, H-2), 7.36–7.30 (3 H, m, H-4′, H-6′), 6.90–6.87 (1 H, m, H-2′), 6.86–6.83 (2 H, m, H-3), 6.23 (1 H, dd, *J* = 15.9, 8.4 Hz, H-1′), 4.65 (1 H, d, *J* = 1.9 Hz, H_a), 4.63 (1 H, ddd, *J* = 8.4, 1.9. 0.6 Hz, H_b), 3.76 (3 H, s, OCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.9 (C=O), 156.8 (C-4), 136.4 (C-2′), 135.1 (C-3′), 130.7 (C-1), 128.9 (C-6′), 128.8 (C-4′), 126.9 (C-5′), 123.6 (C-1′), 118.9 (C-2), 114.5 (C-3), 65.3 (C_b), 61.4 (C_a), 55.5 (OCH_3).

Methyl 2-[*trans*-3-Chloro-4-(4-fluorophenyl)-4-oxoazetidin-1-yl]acetate (7p′)

Yellow oil; yield: 570.6 mg (82%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.36 (2 H, m, H-2′), 7.14–7.11 (2 H, m, H-3′), 4.90 (1 H, d, *J* = 1.9 Hz, H_a), 4.60 (1 H, d, *J* = 1.9 Hz, H_b), 4.36 (1 H, d, *J* = 18.1 Hz, H-2α, H-2β), 3.72 (3H, s, OCH_3), 3.58 (1 H, d, *J* = 18.0 Hz, H-2α, H-2β).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.7 (C-1), 164.3 (*J* = 248.9 Hz, C-4′), 163.8 (C=O), 130.3 (*J* = 3.8 Hz, C-1′), 128.7 (*J* = 8.5 Hz, C-2′), 116.3 (*J* = 21.8 Hz, C-3′), 65.2 (C_b), 63.5 (C_a), 52.4 (OCH_3), 41.6 (C-2).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $[C_{12}H_{12}ClFNO_3]^+$: 272.0489; found: 272.0461.

Methyl 6-[*trans*-3-Chloro-4-(4-fluorophenyl)-4-oxoazetidin-1-yl]hexanoate (7q′)

Yellow oil; yield: 521.7 mg (80%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 (2 H, dd, *J* = 8.6, 5.2 Hz, H-2′), 7.13 (2 H, t, *J* = 8.5 Hz, H-3′), 4.53 (1 H, d, *J* = 1.4 Hz, H_a), 4.47 (1 H, d, *J* = 1.1 Hz, H_b), 3.66 (3 H, s, OCH_3), 3.24–3.13 (2 H, m, H-6), 2.59 (2 H, t, *J* = 7.4 Hz, H-2), 1.70–1.55 (4 H, m, H-3, H-5), 1.52 (2 H, dt, *J* = 14.8, 7.4 Hz, H-4).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.8 (C-1), 161.7 (C=O), 160.3 (*J* = 246.4 Hz, C-4′), 131.0 (*J* = 2.6 Hz, C-1′), 128.4 (*J* = 8.4 Hz, C-2′), 116.4 (*J* = 21.9 Hz, C-3′), 65.4 (C_b), 63.1 (C_a), 51.6 (OCH_3), 40.9 (C-6), 33.7 (C-2), 27.1 (C-5), 26.3 (C-4), 24.3 (C-3).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $[C_{16}H_{20}ClFNO_3]^+$: 328.1115; found: 328.1078.

3,3-Dichloro-1-(4-methoxyphenyl)-4-(4-nitrophenyl)azetidin-2-one (7r)

Yellow oil; yield: 651.9 mg (91%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.28 (2 H, d, *J* = 6.6 Hz, H-3′), 7.52 (2 H, d, *J* = 6.8 Hz, H-2′), 7.21 (2 H, d, *J* = 6.8 Hz, H-2), 6.84 (2 H, dd, *J* = 8.9, 2.1 Hz, H-3), 5.60 (1 H, s, H_b), 3.76 (2 H, s, OCH_3).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 157.7 (C=O), 157.2 (C-4), 148.9 (C-4′), 138.9 (C-1′), 128.9 (C-2′), 128.6 (C-1), 124.3 (C-3′), 119.4 (C-2), 114.9 (C-3), 83.8 (CCl_2), 72.9 (C_b), 55.6 (OCH_3).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $[C_{16}H_{12}Cl_2N_2O_4]^+$: 366.0174; found: 366.0168.

3,3-Dichloro-1,4-bis(4-methoxyphenyl)azetidin-2-one (7s)

White solid; yield: 605.8 mg (83%); mp 128–130 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.26 (4 H, dd, *J* = 12.9, 5.7 Hz, H-3, H-3′), 6.95 (2 H, d, *J* = 8.7 Hz, H-2), 6.82 (2 H, d, *J* = 9.0 Hz, H-2′), 5.45 (1 H, s, H_b), 3.82 (3 H, s, C4′-OCH_3), 3.76 (3 H, s, C4-OCH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 160.8 (C=O), 158.0 (C-4′), 157.2 (C-4), 129.3 (C-2′), 129.2 (C-1), 123.5 (C-1′), 119.5 (C-2), 114.6 (C-3), 114.4 (C-3′), 84.6 (CCl_2), 73.8 (C_b) 55.5 (C4′-OCH_3), 55.4 C4-OCH_3).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $[C_{17}H_{14}Cl_2NO_3]^+$: 350.0351; found: 351.0424.

3,3-Dichloro-1-(4-chlorophenyl)-4-(2,4-dichlorophenyl)azetidin-2-one (7t)

Yellow oil; yield: 618.5 mg (89%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.48–7.43 (1 H, m, H-3′), 7.41 (2 H, d, *J* = 8.7 Hz, H-3), 7.31 (2 H, d, *J* = 5.6 Hz, H-5′, H-6′), 7.20 (2 H, d, *J* = 8.7 Hz, H-2), 5.50 (1 H, s, H_b).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.4 (C=O), 134.9 (C-2′), 132.5 (C-3), 131.2 (C-1), 130.2 (C-3′, C-4), 129.2 (C-5′, C-6′), 127.8 (C-1′), 119.7 (C-2), 118.7 (C-4′), 84.2 (CCl_2) 74.2 (C_b).

cis-3-Bromo-1-(4-chlorophenyl)-4-(2,4-dichlorophenyl)azetidin-2-one (7u)

White solid; yield: 270.8 mg (38%); mp 186–187 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.37 (3 H, m, H-3, H-3′), 7.30–7.24 (2 H, m, H-5′, H-6′), 7.21 (2 H, d, *J* = 8.8 Hz, H-2), 5.39 (2 H, s, H_a, H_b).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.1 (C=O), 135.9 (C-2′), 133.3 (C-1), 132.4 (C-3′, C-6′), 129.5 (C-5′), 128.9 (C-3), 127.7 (C-4, C-4′), 119.1 (C-2), 117.8 (C-1′), 59.8 (C_a), 50.4 (C_b).

trans-3-Bromo-1-(4-chlorophenyl)-4-(2,4-dichlorophenyl)azetidin-2-one (7u′)

Yellow oil; yield: 228.0 mg (32%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44–7.39 (2 H, m, H-5′, H-3′), 7.39–7.34 (3 H, m, H-3, H-6′), 7.17 (2 H, d, *J* = 8.8 Hz, H-2), 5.09 (1 H, s, H_a), 4.64 (1 H, d, *J* = 1.9 Hz, H_b).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 160.7 (C=O), 136.0 (C-2′), 134.8 (C-1), 132.3 (C-3′, C-6′), 129.8 (C-5′), 129.7 (C-3), 126.1 (C-4, C-4′), 119.1 (C-2), 117.8 (C-1′), 66.1 (C_a), 50.1 (C_b).

cis-1-(4-Methoxyphenyl)-2-(4-nitrophenyl)-4-oxoazetidin-3-yl Acetate (7v)

Orange oil; yield: 83.4 mg (12%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.23 (2 H, d, *J* = 8.8 Hz, H-3′), 7.50 (2 H, d, *J* = 8.7 Hz, H-2′), 7.23 (2 H, d, *J* = 9.0 Hz, H-2), 6.82 (2 H, d, *J* = 9.1 Hz, H-3), 6.00 (1 H, d, *J* = 5.0 Hz, H_a), 5.45 (1 H, d, *J* = 5.0 Hz, H_b), 3.76 (3 H, s, OCH_3), 1.74 (3 H, s, CO_2CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 169.9 (CO_2CH_3), 160.2 (C=O), 142.3 (C-4′), 129.9 (C-4), 127.5 (C-3′), 124.4 (C-2′), 122.2 (C-1′), 118.8 (C-2), 114.6 (C-3), 114.3 (C-1), 82.4 (C_a), 63.0 (C_b), 55.5 (OCH_3), 20.4 (CO_2CH_3).

***trans*-1-(4-Methoxyphenyl)-2-(4-nitrophenyl)-4-oxoazetidin-3-yl Acetate (7v′)**

Yellow oil; yield: 69.5 mg (10%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.25 (2 H, d, *J* = 6.6 Hz, H-3′), 7.29–7.24 (2 H, m, H-2′), 7.19 (2 H, dd, *J* = 9.1, 2.3 Hz, H-2), 6.81 (2 H, dd, *J* = 9.2, 2.2 Hz, H-3), 5.28 (1 H, s, H_a), 5.00 (1 H, s, H_b), 3.76 (3 H, s, OCH_3), 2.22 (3 H, s, CO_2CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 169.1 (CO_2CH_3), 160.6 (C=O), 140.0 (C-4), 129.7 (C-4′), 128.9 (C-3′), 123.7 (C-2′), 122.2 (C-1′), 118.7 (C-2), 114.7 (C-3), 114.3 (C-1), 76.4 (C_a), 60.7 (C_b), 55.5 (OCH_3), 19.9 (CO_2CH_3).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $[C_{18}H_{16}N_2O_6]^+$: 356.1008; found: 356.1006.

(*Z*)-2-Chloro-3-(4-methoxyphenyl)-1-phenylacrylamide (8b)

White solid; yield: 68.1 mg (10%); mp 167–168 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.50 (1 H, s, NH), 8.07 (1 H, s, H-3), 7.82 (2 H, d, *J* = 8.8 Hz, H-2′), 7.64 (2 H, d, *J* = 7.5 Hz, H-2″), 7.37 (2 H, t, *J* = 7.5 Hz, H-3′), 7.16 (1 H, t, *J* = 7.3 Hz, H-4′), 6.95 (2 H, dt, *J* = 8.9, 2.8 Hz, H-3″), 3.85 (3 H, s, OCH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 161.1 (C-1), 160.5 (C-4″), 137.5 (C-1′), 134.5 (C-3), 132.6 (C-2″), 129.2 (C-3′), 125.8 (C-1″), 125.0 (C-4′), 120.6 (C-2), 120.4 (C-2′), 114.2 (C-3″), 55.5 (OCH_3).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $[C_{16}H_{15}ClNO_2]^+$: 288.0791; found: 288.1411.

(*Z*)-2-Chloro-*N*-(4-nitrophenyl)-3-phenylacrylamide (8e)

White solid; yield: 167.3 mg (25%); mp 167–168 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.80 (1 H, s, NH), 8.28 (2 H, d, *J* = 9.0 Hz, H-3′), 8.16 (1 H, s, H-3), 7.84 (4 H, dd, *J* = 11.7, 8.5 Hz, H-2″, H-2′), 7.46 (3 H, d, *J* = 6.8 Hz, H-3″, H-4″).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.4 (C-1), 144.2 (C-4′), 142.9 (C-1′), 136.3 (C-3), 132.7 (C-1″), 130.6 (C-2″), 130.5 (C-2), 128.7 (C-3″), 125.1 (C-3′), 121.9 (C-4″), 119.7 (C-2′).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $[C_{15}H_{12}ClN_2O_3]^+$: 303.0536; found: 303.0501.

(*Z*)-2-Chloro-*N*-(4-bromophenyl)-3-phenylacrylamide (8f)

Yellow solid; yield: 219.9 mg (34%); mp 125–126 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.51 (1 H, s, NH), 8.12 (1 H, s, H-3), 7.80 (2 H, d, *J* = 6.9 Hz, H-3′), 7.59–7.37 (7 H, m, H-2″, H-3″, H-4″, H-2′).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.0 (C-1), 136.3 (C-4″), 135.3 (C-3), 133.0 (C-1′), 132.1 (C-3′), 130.5 (C-2″), 130.1 (C-2), 128.6 (C-3″), 122.6 (C-1″), 121.8 (C-2′), 117.8 (C-4′).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $[C_{15}H_{12}BrClNO]^+$: 335.9791; found: 335.9750.

(*Z*)-2-Chloro-*N*-(4-chlorophenyl)-3-(2-thiophen-2-yl)acrylamide (8h)

Brown crystals; yield: 262.3 mg (39%); mp 136–137 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.31 (1 H, s, NH), 7.61–7.55 (3 H, m, H-3, H-3′), 7.51 (1 H, d, *J* = 3.7 Hz, H-5″), 7.35–7.30 (3 H, m, H-4″, H-2′), 7.14 (1 H, td, *J* = 5.0, 2.1 Hz, H-3″).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.9 (C-1), 136.6 (C-4′), 135.9 (C-5″), 134.5 (C-1″), 131.2 (C-3), 130.1 (C-1′), 129.2 (C-2′), 129.0 (C-4″), 127.3 (C-3″), 121.5 (C-3′), 119.6 (C-2).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $[C_{13}H_{10}Cl_2NOS]^+$: 297.9860; found: 298.0480.

(*Z*)-2-Chloro-*N*-(4-chlorophenyl)-3-(2-furan-2-yl)acrylamide (8i)

Red solid; yield: 274.4 mg (40%); mp 140–141 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.44 (1 H, s, NH), 8.02 (1 H, s, H-3), 7.60–7.58 (3 H, m, H-3″, H-3′), 7.33 (2 H, d, *J* = 8.6 Hz, H-2′), 7.17 (1 H, d, *J* = 3.2 Hz, H-4″), 6.58 (1 H, s, H-5″).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.7 (C-1), 149.4 (C-1″), 145.0 (C-3″), 135.8 (C-4′), 130.1 (C-2), 129.2 (C-3′), 123.6 (C-1′), 121.4 (C-3), 119.4 (C-2′), 116.6 (C-4″), 112.6 (C-5″).

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $[C_{13}H_{10}Cl_2NO_2]^+$: 282.0089; found: 282.0058.

(*Z*)-2-Chloro-*N*-(4-methoxyphenyl)-3-(4-methoxyphenyl)acrylamide (8k)

White crystals; yield: 79.0 mg (12%); mp 146–147 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.42 (1 H, s, NH), 8.04 (1 H, s, H-3), 7.79 (2 H, d, *J* = 8.8 Hz, H-2′), 7.52 (2 H, d, *J* = 9.0 Hz, H-2″), 6.93 (2 H, d, *J* = 8.9 Hz, H-3′), 6.88 (2 H, d, *J* = 9.0 Hz, H-3″), 3.82 (3 H, s, C4′-OCH_3), 3.78 (3 H, s, C4″-OCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.9 (C-1), 160.3 (C-4″), 156.9 (C-4′), 134.0 (C-3), 132.4 (C-2″), 130.5 (C-1′), 125.8 (C-1″), 122.1 (C-2), 120.6 (C-2′), 114.2 (C-3′), 114.0 (C-3″), 55.5 (C4′-OCH_3), 55.3 (C4″-OCH_3) .

HRMS (ESI+): *m*/*z* [M + Na]$^+$ calcd for $[C_{17}H_{16}ClNO_3Na]^+$: 340.0717; found: 340.0778.

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